

silicon epitaxial films grown by molecular beam epitaxy

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Oxygen-doped Si epitaxial films (OXSEF) grown by molecular beam epitaxy and subsequently implanted with Er show room-temperature luminescence around $\lambda = 1.54 \mu\text{m}$. The 45-nm-thick films have an oxygen concentration of 10 at. % and were implanted with 7.8×10^{14} 25 keV Er ions/cm². The luminescence was optically excited with the 514 nm line of an Ar ion laser and is attributed to intra-4*f* transitions in Er³⁺. Thermal annealing at 700–800 °C is necessary to optimize the luminescence after implantation. Pure Si implanted and annealed under the same conditions does not show Er-related luminescence at room temperature. The emission from Er in OXSEF is attributed to the high concentration of oxygen in the films, which forms complexes with Er. The excitation of Er³⁺ is due to a photocarrier mediated mechanism.

INTRODUCTION

The development of integrated silicon-based optoelectronic technology requires the attainment of efficient light emission from Si. However, the indirect band gap of Si precludes efficient light emission under electrical excitation. To overcome this problem optical doping of Si with erbium has been suggested.^{1,2} Erbium in its trivalent state shows luminescence around 1.54 μm , one of the standard wavelengths in optical communication technology. This characteristic luminescence is a result of intra-4*f* shell transitions in the ion, and since this shell is shielded by the closed 5s²5p⁶ shells the influence of the host lattice is weak. Following the idea of the optical doping, some work^{3,4} has been devoted to the structural aspects of the incorporation of Er in Si, and concentrations as high as 1.2×10^{20} Er/cm³ have been reached.⁴ Nevertheless, the emission from Er has been shown to be very inefficient, and there is virtually no measurable signal at room temperature.^{5,6} Other work has shown the possibility to enhance the luminescence in Er-doped Si by the simultaneous presence of other impurities such as O, C, N, F, or B.^{6–8} In particular, the fraction of optically active Er ions in Czochralski-grown Si (Cz-Si), in which the O content is $\sim 10^{18}/\text{cm}^3$, is much higher than in float zone Si, in which the O content is below $\sim 10^{16}/\text{cm}^3$.⁶ This has been attributed to the modification of the local environment around Er, which would favor the oxidation of Er to the trivalent (luminescent) state. Extended x-ray absorption fine-structure measurements have recently confirmed the formation of Er-O clusters in Er-implanted Cz-Si.⁹ However, even in the most optimized structure, the 1.5 μm luminescence is quenched at room temperature and emission is only observed below ~ 100 K. Therefore the study of the incorporation of Er in a Si-based material with a much higher oxygen concentration is of great interest.

Oxygen-doped epitaxial Si films (OXSEF) grown by molecular beam epitaxy (MBE) have been used for this study. The material has been characterized as a wide-gap semiconductor and can be electrically doped.¹⁰ Further,

the feasibility of fabricating OXSEF/Si heterodiodes has been demonstrated.¹¹ The oxygen content of the films can be several tens of atomic percent,¹⁰ which is far above the equilibrium solid solubility of oxygen in Si (10^{18} cm^{-3} at 1250 °C). The crystal structure of OXSEF has been studied during growth by reflection high-energy electron diffraction and after deposition by cross-sectional high resolution transmission electron microscopy.¹⁰ The results show that the as-grown films are epitaxial on the Si (111) used as a substrate, with a large density of {111} twins. In this paper we study Er doping of OXSEF by ion implantation. After thermal annealing clear room-temperature luminescence around 1.5 μm is observed, which is attributed to a photocarrier-mediated process.

EXPERIMENT

The OXSEF were prepared at the Electrical Communications Laboratories of the Nippon Telegraph and Telephone Corporation, Tokyo. The films were grown using MBE on Si(111) at 500 °C under an oxygen partial pressure $P(\text{O}_2) = 5 \times 10^{-7}$ Torr. The base pressure without O₂ was $\leq 5 \times 10^{-9}$ Torr. The films grown under these conditions have an oxygen concentration of about 10 at. %¹⁰ and a nominal thickness of ~ 48 nm. Further details of the experimental setup and growth procedure can be found in Ref. 10. The implantation was performed in a single-ended Van de Graaf accelerator, using a sputtering source in which pure Er was used as a cathode material and Ne as sputter gas. The OXSEF were implanted at room temperature with 7.8×10^{14} Er ions/cm² at 25 keV. A reference sample of Cz-Si (100) was simultaneously implanted. The pressure during implantation was 10^{-6} Torr.

The OXSEF thickness, and the oxygen and Er profiles were measured with Rutherford backscattering spectrometry (RBS) using 2 MeV He⁺ beam and a scattering angle of 100°. Channeling measurements were done with the ion beam aligned with the [111] direction of the Si(111) substrate. Thermal annealing treatments were performed in a standard tube furnace at pressures below 10^{-7} Torr during

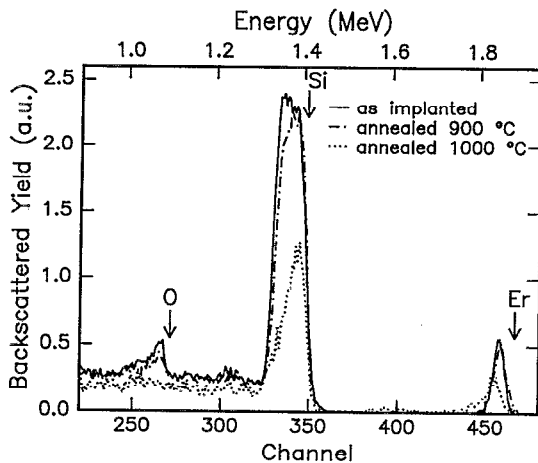


FIG. 1. RBS channeling spectra for Er-implanted OXSEF (7.8×10^{14} Er/cm² at 25 keV), as implanted (solid line), and after annealing for 30 min at 900 °C (dashed line) and at 1000 °C (dotted line). The scattering angle was 100°.

30 min in the temperature range 600–1000 °C. Photoluminescence (PL) spectroscopy was performed using the 514.5 nm line of an Ar ion laser as a pump source. Photoluminescence Excitation (PLE) spectroscopy was performed using various Ar ion laser lines between 457.9 and 514.5 nm. PL and PLE spectra were recorded illuminating the samples with pump powers of 900 and 420 mW, respectively, with the pump beam mechanically chopped at 13 Hz. The luminescence signal was collected using a 0.48 m monochromator, a liquid nitrogen cooled Ge detector, and a lock-in amplifier. The spectral resolution was 6 nm.

RESULTS

Figure 1 shows the RBS channeling spectrum of Er-implanted OXSEF, as implanted and after annealing for 30 min at 900 and 1000 °C. The Si part of the channeling spectrum for the unimplanted sample (not included in the figure) shows no differences when compared to the one of the as-implanted sample. The poor channeling for the as-grown sample is attributed to twins and crystalline imperfections.^{10,12} The OXSEF thickness as determined from the Si part of the RBS spectrum is 45 nm, in good agreement with the given nominal value. The Er implantation does not modify the as-grown oxygen profile. The as-implanted Er profile is approximately Gaussian with a full width at half-maximum of ~ 17 nm and peaks at a depth of ~ 20 nm from the surface. After thermal annealing up to 800 °C the channeling spectra do not show any change in either the OXSEF Si yield or the O and Er profiles (data not shown). After annealing at 900 °C the Er profile remains unchanged (Fig. 1), while the Si yield from the OXSEF has been slightly reduced at the Si/OXSEF interface. A reduction of the oxygen peak is also observed. This effect becomes more pronounced after annealing at 1000 °C: the oxygen signal has been reduced to the background level and the Si yield has decreased significantly. The Er profile has also changed, showing Er displacement

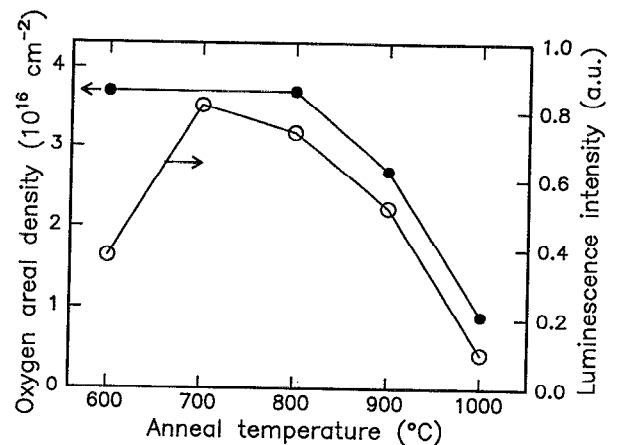


FIG. 2. Oxygen areal density (solid data points, left axis) and room-temperature luminescence intensity at 1.54 μ m (open data points, right axis) as a function of the annealing temperature for Er-implanted OXSEF (7.8×10^{14} Er/cm² at 25 keV). Annealings were performed for 30 min in vacuum.

towards the substrate, and the integrated area is reduced and accounts for 5.0×10^{14} Er/cm². The random spectrum (not shown) of this sample shows no O peak, confirming that there is no oxygen in the film. The Er areal density in the random spectrum is 6.5×10^{14} Er/cm², somewhat higher than in the channeling spectrum but still lower than the as-implanted fluence of 7.8×10^{14} Er/cm², suggesting that some Er has been lost.

In Fig. 2 the evolution of the oxygen content as measured by RBS is plotted as a function of the annealing temperature (solid data points, left axis). Up to 800 °C the concentration is equal to that of the as-grown film, and for higher anneal temperatures it decreases monotonously, to reach a small value after 1000 °C annealing.

Figure 3 shows the room-temperature luminescence spectrum for Er-implanted OXSEF after annealing at 700 °C for 30 min. The spectrum shows clear peaks around 1.54 μ m, characteristic of transitions between the $^4I_{13/2}$ and $^4I_{15/2}$ manifolds in Er³⁺. Also included in the figure is

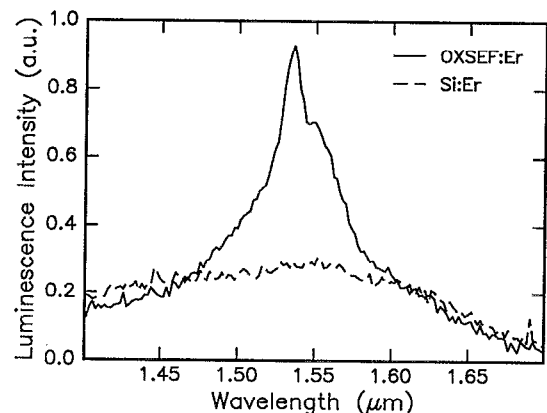


FIG. 3. Luminescence spectra at room temperature for Er-implanted OXSEF and Cz-Si (7.8×10^{14} Er/cm² at 25 keV) after annealing for 30 min at 700 °C. The 514.5 nm line of an Ar ion laser was used as an excitation source.

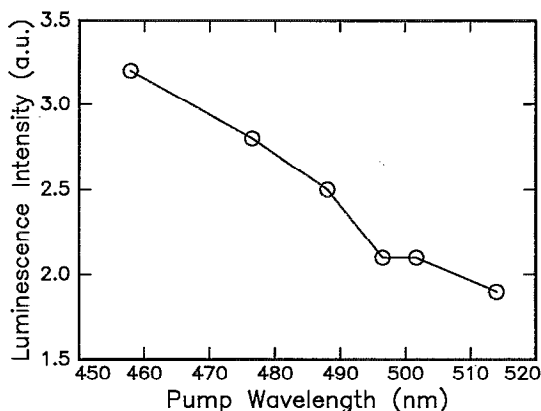


FIG. 4. Room-temperature luminescence peak intensity at $\lambda = 1.54 \mu\text{m}$ vs pump wavelength for Er-implanted OXSEF (7.8×10^{14} Er/cm² at 25 keV) after annealing for 30 min at 700 °C in vacuum.

the luminescence spectrum of a Cz-Si sample implanted and annealed under the same conditions. This sample shows no Er-related luminescence and only a broad background signal is observed, attributed to implantation-induced defects in Si.¹³ In Fig. 2 the dependence of the Er-related luminescence peak intensity at $1.54 \mu\text{m}$ in OXSEF is shown as a function of annealing temperature (open data points, right axis), together with the oxygen content in the films. The luminescence increases to reach a maximum around 700–800 °C and then decreases sharply for higher anneal temperatures, as the oxygen content is reduced. No Er-related signal is left after annealing at 1000 °C.

To get further insight into the Er³⁺ excitation mechanism in OXSEF, PLE spectroscopy was performed. Figure 4 shows the luminescence peak intensity at $1.54 \mu\text{m}$ as a function of the pump wavelength for the sample annealed at 800 °C. A gradual decrease with pump wavelength is observed, with no further structure.

DISCUSSION

The RBS channeling spectra after annealing up to 800 °C do not show differences when compared to the as-implanted spectrum, either in the Si part or in the Er profile. This observation is different from the one reported for Er-implanted single-crystal Si.⁴ In that case Er implantation leads to amorphization of a surface layer, which during annealing at 600 °C recrystallizes epitaxially with some Er segregating to the surface. In the OXSEF the poor channeling observed for the as-grown sample, due to crystalline imperfections, does not allow us to study possible amorphization and recrystallization processes with RBS analysis. However, the slight decrease in Si yield near the Si/OXSEF interface after the 900 °C annealing is indicative of some epitaxial realignment. Indeed, oxygen is known to retard the solid-phase epitaxy rate of Si,¹⁴ and therefore annealing at higher temperatures may be required for some alignment to take place. The fact that no segregation of Er is observed in OXSEF after annealing up to 900 °C is in

agreement with a recent observation that coimplanted oxygen greatly reduces the segregation of Er in pure Si during annealing.¹⁵

After annealing at 1000 °C nearly all oxygen is lost and further alignment of the Si is observed. The minimum yield is still high, indicating the presence of many defects in the layer regrown from the OXSEF/Si interface. This observation agrees with the behavior reported in a previous study of thin (~ 7 nm) OXSEF by medium-energy ion scattering in which it was found that the films were stable up to 800 °C.¹² The decrease in Si yield was explained by a reduction in defect density and strain as the oxygen is lost, possibly by out-diffusion and/or evaporation. The somewhat higher temperature limit found in the present work for the complete out-diffusion of O may be due to the larger thickness of the film (~ 45 nm). The Er profile for the 1000 °C annealed sample shows that Er diffusion has taken place towards the Si substrate. The comparison between the areal density in the random and channeling spectra indicates that 15% of the Er is lost either into the bulk or by evaporation, while the remaining 85% partially resides in a well-defined position in the Si lattice.

The increase of the luminescence intensity in the annealing range up to 700 °C can be attributed to both the annealing of implantation-induced defects which quench the luminescence, and an increase in the fraction of optically active Er³⁺ ions through complex formation with oxygen. The decrease of the luminescence intensity in the annealing range from 800 to 1000 °C seems to be related to the decreasing oxygen content in the film. The fact that Er luminescence is observed in OXSEF at room temperature, while it is not observed for Cz-Si can be due to several reasons: the higher oxygen concentration may (1) increase the active (i.e., trivalent) Er fraction, (2) reduce the luminescence quenching at room temperature, or (3) may have an advantageous effect on the excitation efficiency. Further measurements are underway to distinguish between these three effects.

The PLE spectrum shows a gradual decrease of the luminescence with increasing pump wavelength, implying that the excitation of Er³⁺ does not result from direct absorption of the pump light by the ions. In that case, relatively narrow absorption bands should be observed around 488 and 514.5 nm, corresponding to the $^4I_{15/2} \rightarrow ^4F_{7/2}$ and $^4I_{15/2} \rightarrow ^2H_{11/2}$ transitions in Er³⁺, respectively. Indeed, such peaks have been observed in Er-implanted SiO₂.¹⁶ The result shown in Fig. 4 therefore indicates that the Er ions are excited through photogenerated carriers, created either in the OXSEF or in the Si substrate. The monotonic decrease of the luminescence as a function of the wavelength in OXSEF can be explained by the decrease in optical absorption coefficient for larger pump wavelengths, assuming that the optical behavior of OXSEF is similar to that of Si.¹⁷ This decrease in absorption both in the film and in the Si will lead to a decrease in the number of the photogenerated carriers in or near the OXSEF, resulting in less efficient excitation of Er. It is important to note that the $1/e$ penetration depth of the pump wavelength is 890 nm in (defect free) *c*-Si,¹⁸ and

therefore only a very small fraction of the incident light is absorbed in the 45-nm-thick film. As clear luminescence is observed this means the excitation mechanism is rather efficient.

Finally, it is interesting to compare these results with our very recent work on Er-implanted semi-insulating polycrystalline silicon (SIPOS), grown by chemical vapor deposition.¹⁶ This material also shows room-temperature luminescence from Er, excited through a photocarrier-mediated process. However the microstructure of SIPOS and OXSEF is quite different: while SIPOS consists of Si crystalline nanograins surrounded by oxide shells, in OXSEF the oxygen is more homogeneously distributed.¹⁰ Despite this difference, the optical properties and excitation mechanism of Er appear to be very similar.

CONCLUSIONS

OXSEF grown by MBE, and implanted with Er show room-temperature luminescence at 1.54 μm . The maximum luminescence intensity is found after thermal annealing at 700–800 °C. Annealings at higher temperatures (900–1000 °C) lead to out-diffusion and/or evaporation of O, together with a decrease of the luminescence intensity. For Cz-Si implanted and annealed under the same conditions no Er-related room-temperature luminescence is observed. The efficient room-temperature luminescence of Er in OXSEF is attributed to the high concentration of oxygen in the films (10 at. %), which forms complexes with Er. The Er excitation mechanism is via a photocarrier mediated process. Er-doped OXSEF is a promising material for integrated optoelectronics.

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